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Open-File Report 2004-1326

U.S. Department of the Interior
U.S. Geological Survey

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Abstract

The U.S. Geological Survey (USGS) sampled multiple stream sites across the St. Joseph and Galien River Basins to detect and quantify the herbicide atrazine using a field enzyme-linked immunosorbent assay (ELISA) triazine test. In May 2001, July 2001, April 2002, August 2002, August 2003 and September 2003, composite samples were collected across streams at USGS streamflow-gaging stations. Concentrations and instantaneous loading for atrazine sampled in stream water throughout the St. Joseph River and Galien River Basins in Michigan and Indiana ranged from nondetection (< 0.05 part per billion (ppb)) with an associated load less than 0.001 kilogram per day (kg/d) to 6 ppb and a maximum load of 10 kg/d. Atrazine concentrations were highest in May 2001 just after the planting season. The lowest concentration was found in April 2002 just before planting. Atrazine concentrations in streambed-sediment pore water were not spatially connected with atrazine concentrations in stream-water samples. This study showed that atrazine concentrations were elevated from May to July in the St. Joseph and Galien River Basins. At many sites, concentrations exceeded the level that has been shown to feminize frog populations (0.2 ppb). There were 8 sites where concentrations exceeded 0.2 ppb atrazine in May 2001 and July 2001.

Introduction

In 1994-95, the input of atrazine to Lake Michigan from surface-water tributaries was estimated to be 1,600-9,000 kilogram per year, (kg/y) and this loading was 76 percent of the total loading to the lake (U.S. Environmental Protection Agency, 2000a). Although the St. Joseph River contributed less than 10 percent of the surface-water input to the lake, it contributed the largest load of atrazine, 43 percent of the total, to Lake Michigan in 1994-95 (U. S. Environmental Protection Agency, 2000a).

The Lake Michigan Lakewide Management Plan, or LaMP (U.S. Environmental Protection Agency, 2000b), identified atrazine as an emerging pollutant. Atrazine was registered for use in 1959; between 1987 and 1989, it was the most heavily used herbicide in the United States (U.S. Environmental Protection Agency, 2000b). The half-life for atrazine in soil is estimated to be 60 days (Barbash and Resek, 1996). Atrazine degradation, however, appears to occur primarily under aerobic conditions, and the half-life of atrazine under anoxic or anaerobic conditions, which are expected for ground-water systems, may be much greater than 60 days (Barbash and Resek, 1996).

Prolonged exposure to atrazine and related triazines may cause cardiovascular or reproductive difficulties (U.S. Environmental Protection Agency, 2000b). Atrazine also is considered a potential carcinogen (U.S. Environmental Protection Agency, 2000b). For these reasons, the U.S. Environmental Protection Agency (USEPA) has set the maximum contaminant level (MCL) for atrazine at 3 ppb (U.S. Environmental Protection Agency, 2000b) under the National Primary Drinking Water Regulations of the Safe Drinking Water Act.

Hayes and others (2002) reported laboratory and field studies that implied a feminization of frog populations in the wild when frog larvae were exposed to atrazine. They examined eight field sites and reported that all sites associated with atrazine sales exceeding 0.4 kilogram per square kilometer, (kg/km^2) and with waterborne atrazine contamination greater than 0.2 ppb were found to contain males with testicular oocytes. Atrazine sales are used as a surrogate to field loading because field application rates do not have to be reported in all areas. Results and conclusions of the study by Hayes and others (2002) have been questioned (Renner, 2002); nevertheless, atrazine sales in the St. Joseph River Basin greatly exceed the 0.4 kg/km^2 value identified by Hayes and others (2002). An estimate by the U.S. Geological Survey of atrazine application in the basin in 1992 ranges from 3 to more than 10 kg/km^2 atrazine applied (U.S. Geological Survey, 1998).

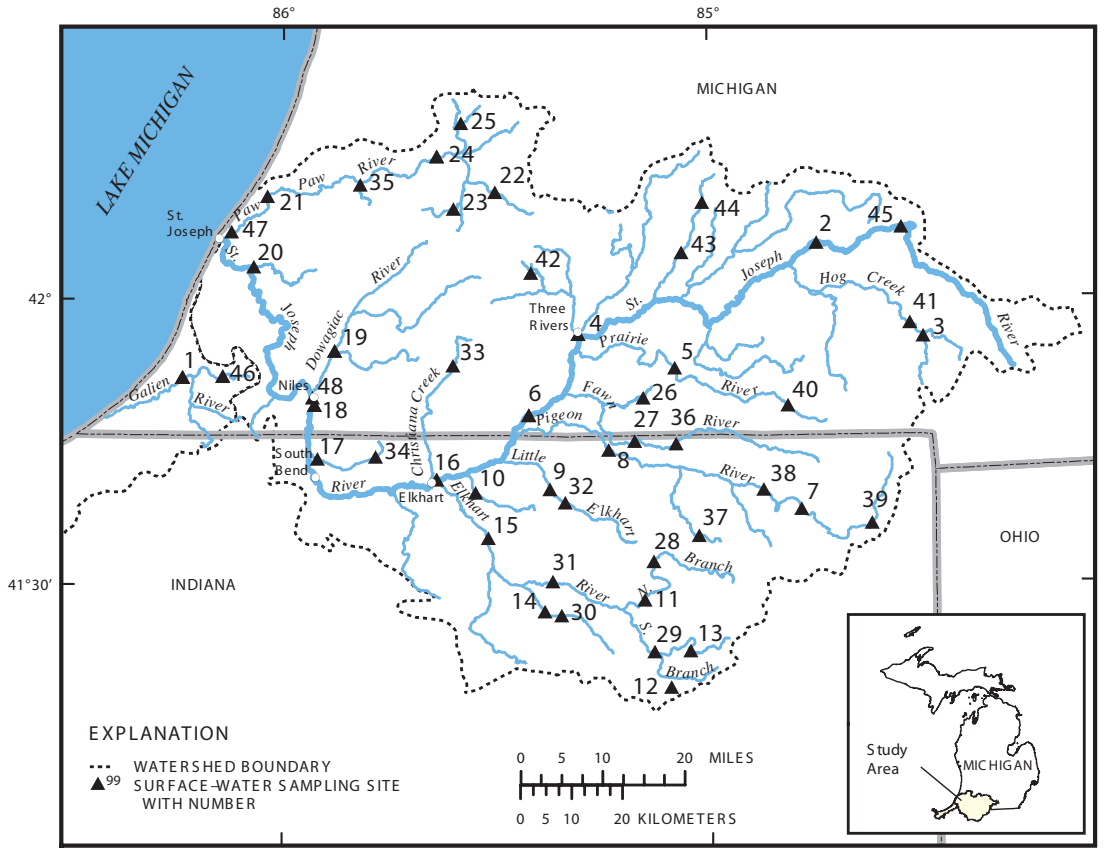

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Figure 1. Surface-water sampling sites in the St. Joseph and Galien River Basins, Michigan and Indiana. Site numbers refer to U.S. Geological Survey sites summarized in table 1.

In 2001, the Michigan and Indiana Districts of the USGS began an investigation of ground-water/surface-water interaction in the St. Joseph River Basin (fig. 1) and to test the use of detailed three-dimensional geologic mapping of glacial deposits in the generation of numerical models to study ground-water/surface-water interaction. As a parallel effort, USGS has completed several reconnaissance samplings for atrazine in the St. Joseph River Basin.

The St. Joseph River is a major exporter of atrazine to Lake Michigan (U.S. Environmental Protection Agency, 2000b), and ground water is an important component of the river flow. However, no direct evidence has been collected of the role of ground water in the delivery of atrazine to surface water and to Lake Michigan. An understanding of the mechanisms controlling atrazine transport in the basin is important, as this information may be used by water-resources managers to reduce atrazine loading in Lake Michigan.

Purpose and Scope

The purpose of this study was to determine whether atrazine was present in stream water within the two basins and to establish whether local high atrazine concentrations could be identified as a first step in understanding the relation of ground water and surface water in atrazine transport. Spatial and temporal variations of atrazine concentrations were examined, as well as methodologies to investigate pore-water/stream-water interactions.

This report summarizes atrazine concentration and load data for samples collected in the St. Joseph River and Galien River Basins from May 2001 to September 2003 as a part of two independent studies. Additional water-quality data collected simultaneously at some of the sampling sites also are presented.

Description of Study Area

The St. Joseph River flows through glacially deposited sediments and has a drainage area of 12,100 km^2. From 80 to 90 percent of its flow is attributable to ground-water discharge (Holtschlag and Nicholas, 1998). The annual mean daily discharge of the St. Joseph River to Lake Michigan is approximately 100 cubic meters per second, (m^3/s) (Blumer and others, 2002), whereas the annual mean daily surface runoff to Lake Michigan from all contributing land surfaces is approximately 1200 m^3/s (Croley and others, 2001). The dynamics of atrazine transport from ground to surface water, however, is unknown. Land use in the basin is dominated by agriculture (71 percent) and forest (16 percent), with 5 percent urban, 6 percent wetland, and 2 percent other land-use (USGS, 1992).

The Galien River also flows through glacially deposited sediments and has a drainage area of 332 square km^2. Mean daily discharge (calendar year) measured at the Galien River near Sawyer, Mich. site is 1.4 m^3/sec. Land use in the Galien Basin is predominantly agricultural (62 percent) and forest (19 percent), with 4 percent urban, 8 percent wetland and 7 percent other land-use (USGS, 1992).

Atrazine transport to the rivers is likely influenced by local geology, irrigation distribution, rainfall events, and the timing and concentrations of atrazine application. If ground-water transport plays a major role in atrazine distribution, management plans that focus on surface runoff to limit atrazine migration in the environment may not be effective because groundwater could take several years to transport atrazine into surface water (Lindsey and others, 2003). In addition, atrazine load reduction goals for Lake Michigan with targets of five to ten years may not be feasible due to long ground-water transport times.

Methods and Approach

This study was composed of two components, (fig 2) each designed to address an individual question. First, is atrazine present in the St. Joseph and Galien River Basins and if so at what concentrations? Second, are there any patterns between atrazine concentrations in stream water and streambed pore water? Results of the two components were then combined to assess localized high atrazine concentrations and their distribution throughout the St. Joseph and Galien River Basins. The first component of the study was a reconnaissance investigation designed to assess stream-water atrazine concentrations and, in some locations, stream-water atrazine loads to Lake Michigan. This component took place from May 2001 to September 2003. The second component of this study, which took place in September 2002, was a comparison of atrazine concentrations in streambed pore water and stream water to test methodologies and assess pore-water/stream-water interaction with regard to atrazine concentration. These studies were then synthesized and the data summarized to assess atrazine concentrations and loads throughout the two basins.

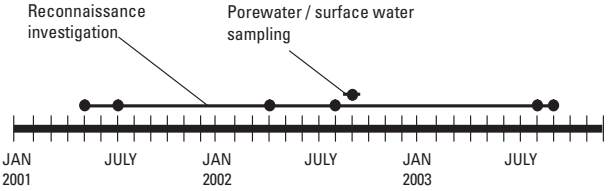

Figure 2. Timeline depicting two components of atrazine study in the St. Joseph and Galien River Basins, Michigan and Indiana. Black dots represent months during which samples were collected.

Reconnaissance Investigation

Two reconnaissance investigations took place to assess atrazine concentrations in the St. Joseph and Galien River Basins. One study was conducted from 2001-2002 and another was conducted in 2003. There were slightly different methods used in each study as described below.

2001-2002

Atrazine concentrations in stream water were determined from samples collected at 21 sites across the St. Joseph River and Galien River Basins in May and July 2001 and April and August 2002 (fig. 2, table 1). The samples were collected primarily at operating USGS stream gaging stations so that the discharge at the sampling site could be easily obtained and the instantaneous atrazine load determined. The only exceptions were samples collected on Pipestone Creek at River Road near Sodus, Mich. (no streamflow-gaging station) and at Rimmell Branch near Albion, Ind. (streamflow-gaging station discontinued in 2001). One set of samples was collected at the Galien River near Sawyer, Mich. (site 1 on fig. 2, table 1), which is outside of the St. Joseph River Basin, in an effort to compare atrazine concentrations across watersheds.

At each site, grab samples were collected with a galvanized bucket lowered on a rope from the bridge crossing the stream. Grab samples were typically taken at several locations across the stream. The samples were composited in a Teflon bottle, and the composite was then collected into an amber glass bottle and stored on ice in a cooler until analysis. All of the sampling equipment was cleaned and was rinsed with methanol between sampling sites (Wilde and others, 1998). At each site, the sampling equipment and sample bottles were rinsed with the stream water before the sample was collected. A multiparameter meter was used to measure temperature, pH, specific conductance, and dissolved oxygen at the sampling locations across each stream. If the meter indicated a large change in any or all of the four measured parameters across the section, then separate stream-water samples would be collected at that site; however, variations in the four parameters were slight enough across all sections that it was not necessary to collect multiple atrazine samples. The

Table 1. Site locations and dates sampled during atrazine study, in the St. Joseph and Galien River Basins, Michigan and Indiana

[USGS, U.S. Geological Survey]

Map number	USGS station name	USGS station number	Latitude	Longitude	Study years
1	Galien River near Sawyer, Mich.	04096015	41°51′25″	86°34′30″	2001, 2002, 2003
2	St. Joseph River at Burlington, Mich.	04096405	42°06′11″	85°04′48″	2001, 2002
3	South Branch Hog Creek near Allen, Mich.	04096515	41°56′55″	84°49′40″	2001, 2002
4	St. Joseph River at Three Rivers, Mich.	04097500	41°56′25″	85°37′58″	2001, 2002
5	Prairie River near Nottawa, Mich.	04097540	41°53′18″	85°24′34″	2001, 2002
6	St. Joseph River at Mottville, Mich .	04099000	41°48′03″	85°45′22″	2001, 2002, 2003
7	Pigeon Creek near Angola, Ind.	04099510	41°38′04″	85°06′35″	2001, 2002
8	Pigeon River near Scott, Ind.	04099750	41°44′56″	85°34′35″	2001, 2002
9	Little Elkhart River at Middlebury, Ind.	04099808	41°40′31″	85°42′01″	2001, 2002
10	Pine Creek near Elkhart, Ind.	04099850	41°40′53″	85°52′02″	2001, 2002
11	North Branch Elkhart River at Cosperville, Ind.	04100222	41°28′54″	85°28′32″	2001, 2002
12	Forker Creek near Burr Oak, Ind.	04100252	41°19′58″	85°25′25″	2001, 2002
13	Rimmell Branch near Albion, Ind.	04100295	41°23′07″	85°22′14″	2001, 2002
14	Solomon Creek near Syracuse, Ind.	04100377	41°27′30″	85°43′12″	2001, 2002
15	Elkhart River at Goshen, Ind.	04100500	41°35′36″	85°50′55″	2001, 2002
16	St. Joseph River at Elkhart, Ind.	04101000	41°41′30″	85°58′30″	2001, 2002
17	Juday Creek near South Bend, Ind.	04101370	41°43′43″	86°15′46″	2001, 2002
18	St. Joseph River at Niles, Mich.	04101500	41°49′45″	86°15′35″	2001, 2002
19	Dowagiac River at Sumnerville, Mich.	04101800	41°54′48″	86°12′47″	2001, 2002
20	Pipestone Creek at River Road near Sodus, Mich.	041020625	42°03′38″	86°24′04″	2001, 2002
21	Paw Paw River at Riverside, Mich.	04102500	42°11′10″	86°22′06″	2001, 2002
22	East Branch Paw Paw River at 28th Street near Mattawan, Mich.	04102172	42°11′40″	85°49′24″	2002
23	Eagle Lake Drain at 39th Street near Lawton, Mich.	04102139	42°09′46″	85°55′35″	2002
24	Paw Paw River at 44th Avenue near Paw Paw, Mich.	04102324	42°15′31″	85°58′06″	2002, 2003
25	Brandywine Creek at 37th Street near Gobles, Mich.	04102240	42°18′52″	85°54′28″	2002
26	Sherman Mill Creek at Sherman Mills Road. near Sturgis, Mich	04098610	41°49′41″	85°28′42″	2002
27	Fawn River at 400 West Road near Scott, Ind.	04098465	41°45′23″	85°30′21″	2002
28	North Branch Elkhart River at 700 South Road. near Eddy, Ind	04100122	41°32′25″	85°27′33″	2002
29	South Branch Elkhart River at River Road near Albion, Ind.	04100303	41°23′10″	85°27′08″	2002
30	Solomon Creek at County Road 43 near Ligonier, Ind.	041003747	41°26′39″	85°40′23″	2002
31	Elkhart River at Highway 13 near Millersburg, Ind.	04100372	41°30′28″	85°41′36″	2002
32	Little Elkhart River at 50 North Road near . Middlebury, Ind	04099804	41°38′49″	85°39′36″	2002
33	Christiana Creek at Brownsville Street near Vandalia, Mich.	04099962	41°53′08″	85°55′38″	2002
34	Juday Creek at Bittersweet Road near Granger, Ind.	414331086063801	41°43′31″	86°06′38″	2002
35	Hog Creek at 62nd Street near Hartford, Mich.	04102405	42°12′20″	86°08′50″	2002
36	Fawn River at 125 East Road near Howe, Ind.	04098325	41°45′01″	85°24′20″	2002
37	Fly Creek at County Road 400 East near LaGrange, Ind.	04099662	41°35′04″	85°20′54″	2002
38	Pigeon Creek at County Road 1175E near Orland, Ind.	04099522	41°40′04″	85°11′29″	2002
39	Pigeon Creek near Hamilton, Ind.	04099070	41°36′16″	84°56′32″	2002
40	Prairie River at Snow Prairie Road near . Bronson, Mich	040975253	41°48′50″	85°08′09″	2002
41	South Branch Hog Creek at Boone Road near Quincy, Mich.	04096520	41°57′44″	84°50′26″	2002
42	Four County Drain at Bowers Road near Flowerfield, Mich.	040973493	42°02′57″	85°44′36″	2002
43	Little Portage Creek at 38th Street near Fulton, Mich.	04097060	42°05′19″	85°23′29″	2002
44	Little Portage Creek at S Avenue near Climax, Mich.	04097038	42°10′22″	85°20′12″	2002
45	St. Joseph River at Twenty-two Mile Road near . Clarendon, Mich	04096340	42°07′51″	84°51′56″	2002
46	East Branch Galien River at Gardener Road near Glendora, Mich.	04095995	41°52′23″	86°28′30″	2003
47	Paw Paw River at North Shore Drive, near Benton Harbor, Mich.	04102521	42°07′32″	86°27′18″	2003

instantaneous gage height was read at each site from a USGS wire-weight gage mounted on a bridge or from the electric tape in the USGS streamflow-gaging station house. The instantaneous gage height was used to determine the instantaneous discharge for the stream from gage height-discharge ratings (Rantz and others, 1982).

Atrazine was measured by means of an ELISA technique (enzyme linked immunosorbent assay). Concentrations were typically measured the day of collection. All samples were stored on ice until analysis (Strategic Diagnostics Inc, 1999). The concentration reported for the ELISA analysis includes atrazine and related triazines (atrazine, propazine, ametryn, prometryn, prometon, desethyl atrazine, terbutryn, terbutylazine, simazine, desisopropyl atrazine, cyanazine, and 2-hydroxy atrazine). In July 2001, two samples were sent to the USGS National Water Quality Laboratory for pesticide screening analysis by means of C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry (Zaugg and others, 1995).

Quality-control techniques included field calibration of the multiparameter meter and field checking of the instrument against standards. Field blank samples were used to check sample handling and preparation steps of the analysis, none of which indicated external contamination of samples. Typically, the ELISA analysis was performed in triplicate on all regular and field blank samples.

2003

In August 2003, stream water was collected at four sites in the St. Joseph River Basin and two sites in the Galien River Basin (table 1); many of these sites were ungaged sites. The Galien River sites were also sampled in September 2003. The Galien River sites were used as a spatial reference, but were also chosen in this part of the reconnaissance investigation because they were on a State of Michigan Total Maximum Daily Load (TMDL)-listed reach. Water samples were collected by use of USGS equal-width-integrated (EWI) sampling procedures (Webb and others, 1999). The EWI fractions were collected in a Teflon collection bottle and composited in a high-density polyethylene (HDPE) churn (Webb and others, 1999). Composite samples were then dispensed in sterile HDPE bottles and stored in the dark, on ice, until analysis (no more than 24 hours after sample collection). These samples were sent to the USGS National Water Quality Laboratory for pesticide screening analysis using C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry (Zaugg and others, 1995).

Measurement of Atrazine Concentrations in Stream water and Streambed Sediment Pore Water

In September 2002, pore water and stream water were collected at 28 sites, most of which are ungaged, in the St. Joseph River Basin (table 1). The purpose of this sampling was to test the methods used to extract streambed-sediment pore water and to identify sites for future intensive sampling to quantify ground-water/stream-water exchange. A steel drive-point piezometer was driven into the streambed to a depth of 20 cm. Pore water was extracted from the streambed though the piezometer with low-density polyethylene (LDPE) tubing and a 30-mL syringe connected by Luer-lock fittings (U.S. Geological Survey, 2000). Typically, 3 to 5 mL of pore water was withdrawn from the streambed and discarded before the sample was collected. The sample was collected into a 1.5-mL amber vial with a screw-top, Teflon-lined cap, and stored on ice until analysis. Several stream- and pore-water samples were collected at each site.

Atrazine Concentrations in Stream Water and Streambed Sediment Pore Water

Results from the two reconnaissance investigations from 2001-2002 and in 2003 are presented below. They are presented separately to accommodate the slightly different methods used in each study.

Reconnaissance Investigation

2001-2002

Spatial distributions of stream-water atrazine concentrations from May 2001, July 2001, April 2002, and August 2002 are shown in figures 3 through 6. Atrazine concentrations in May 2001 were the largest observed in the four sets of samples (fig. 3).

Atrazine is generally applied during or shortly after planting. In the St. Joseph and Galien River Basins, corn is usually planted in late April or early May. The May 2001 samples were collected when many fields were being planted or had just been planted. The maximum atrazine concentration measured was 5.95 ppb at the Galien River near Sawyer, Mich. (site 1).

The only site where the atrazine concentration was below the detection limit of 0.05 ppb during the May 2001 sampling was at the Paw Paw River at Riverside, Mich. (site 21). Atrazine detections were scattered across the basin, and no strong spatial pattern was evident. Of the 21 sites, 17 had concentrations greater than 0.2 ppb, which is the concentration identified by Hayes and others (2002) as leading to feminization of male frogs in the wild.

Atrazine concentrations generally were lower in the July 2001 samples (fig. 4) than in the May 2001 samples. At five sites, concentrations were below the detection limit. The maximum concentration observed was 2 ppb at the Pigeon River near Scott, Ind. (site 8). Samples from nine sites had concentra-

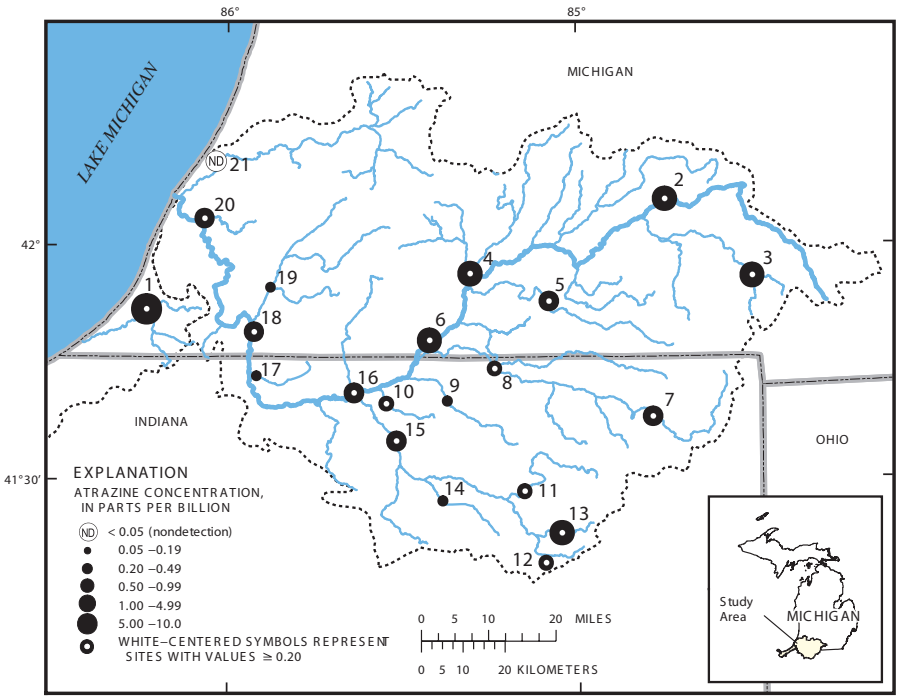

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Figure 3. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, May 2001. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.

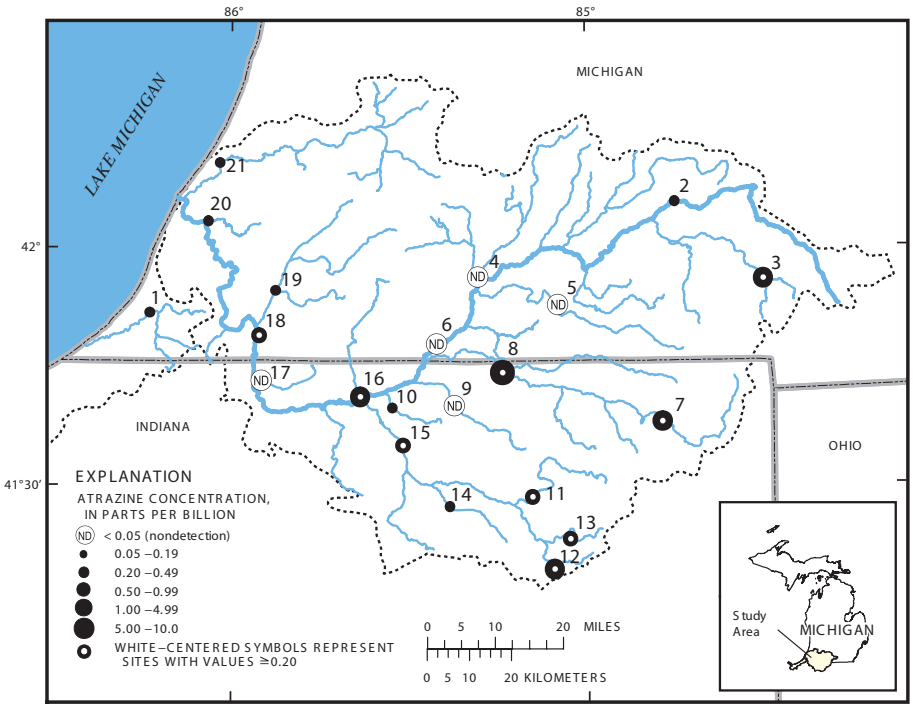

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Figure 4. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, July 2001. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.

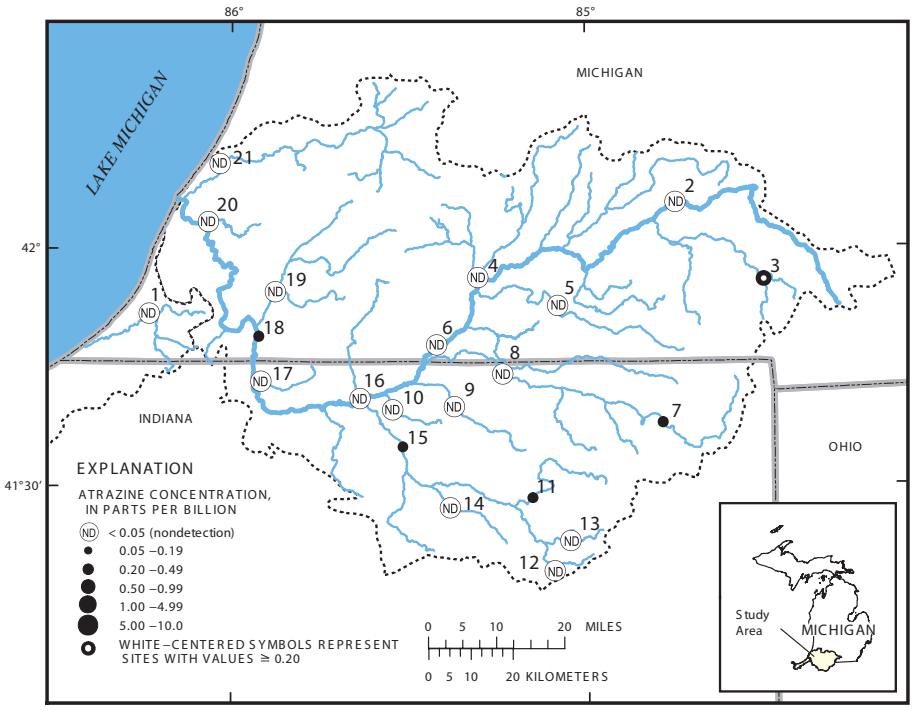

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Figure 5. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, April 2002. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.

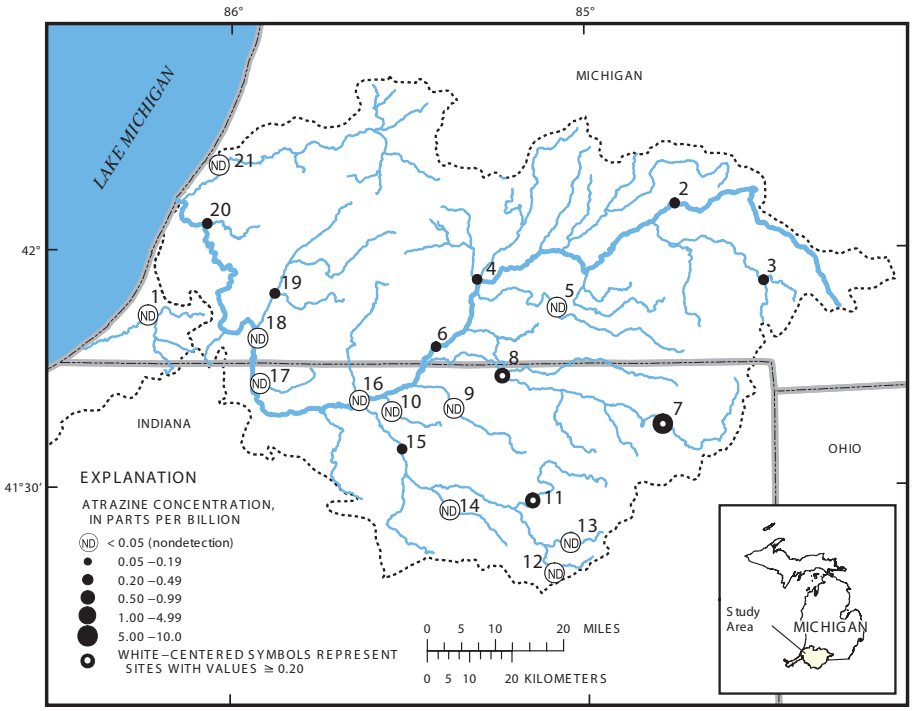

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Figure 6. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, August 2002. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.

tions greater than 0.2 ppb. Concentrations were lower in the Michigan part of the basin than in the Indiana part. Most of the higher concentrations were in the southeast part of the basin. The trend of declining concentration continues for April 2002 samples (fig. 5), which were collected prior to planting. Atrazine concentrations were below detection at 16 sites. The highest concentration was 0.2 ppb at the South Branch of Hog Creek near Allen, Mich. (site 3), and this was the only site with a concentration at the 0.2 ppb level. Detections were scattered across the basin and did not have a spatial pattern.

In August 2002, atrazine concentrations were investigated during low flow. The concentrations followed the general trend shown in the 2001 growing season in that they were between the July 2001 and April 2002 values. Concentrations were below detection level at 11 sites and were greater than 0.2 ppb at only 3 sites. Higher concentrations were found in the southeast part of the basin, although several detections were scattered across the Michigan part of the basin (fig. 6).

Instantaneous loads, computed from the atrazine concentrations and instantaneous discharge at the sites, are shown in figures 7 through 10. The loads followed the concentration pattern, with the largest loads being in May 2001 and the smallest in April and August 2002. Loads were larger in the May 2001 samples because the concentrations were the highest and the instantaneous discharge values were the highest of the four sets of samples. The largest load was 10 kg/d for the St. Joseph River at Niles, Mich. (site 18). The largest loads tended to be at sites along the St. Joseph River because the flow rate of the river is so much greater than most of the tributaries measured, and the concentrations at the St. Joseph River sites vary little (fig. 7-10). The minimum load was less than 0.001 kg/d for several sites during the August 2002 sampling.

2003

Stream-water atrazine concentrations measured in August and September 2003 are shown in figures 11 and 12, respectively. In August, the mean of stream-water concentrations was 0.15 ppb. The minimum atrazine concentration was nondetection at two sites, and the maximum atrazine concentration was 0.35 ppb at St. Joseph River at Niles, Mich. (auxiliary site) (site 48). In September, the mean of stream-water concentrations of atrazine was 0.10 ppb. The minimum concentration was 0.08 ppb at the East Branch Galien River at Gardener Road near Glendora, Mich. (site 46). The maximum concentration of atrazine was 0.12 ppb at the Galien River near Sawyer, Mich. (site 1).

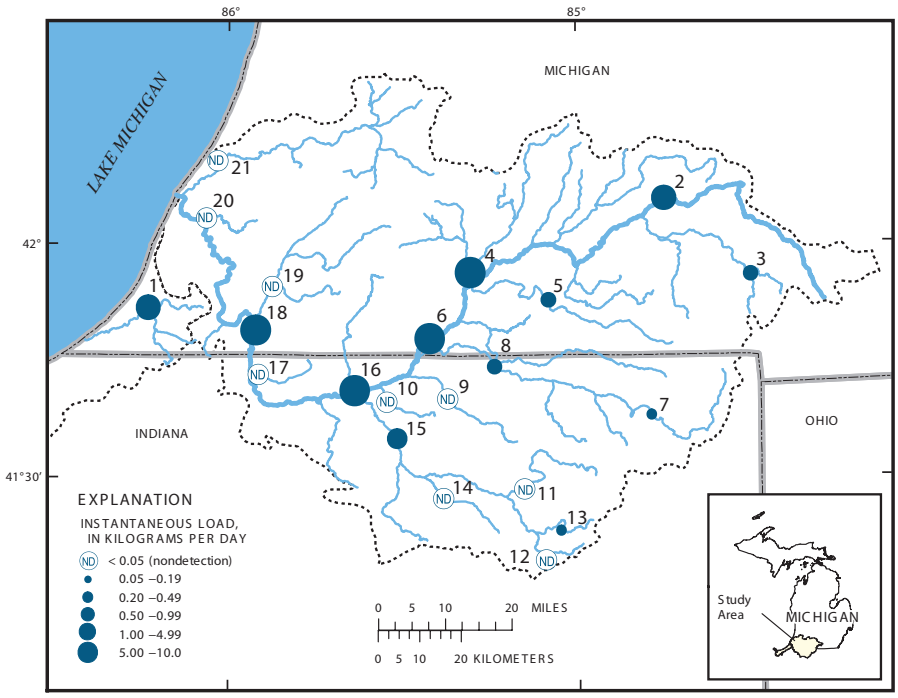
Comparison of Atrazine Concentrations in Stream Water and in Streambed Sediment Pore Water

The stream-water and pore-water concentrations of atrazine measured for the September 2002 sampling are depicted in figures 13 and 14. Arithmetic averages of all stream-water and pore-water atrazine concentrations were 0.21 and 0.20 ppb, respectively. The minimum atrazine concentration was nondetection for pore-water and stream-water samples, and the maximum concentration for stream water and pore water was 0.67 ppb. Despite similarities in average concentrations, the pore-water and stream-water concentration distributions of atrazine were different. Sites with high pore-water concentrations of atrazine did not necessarily correspond to sites with high stream-water concentrations. The differences between pore-water and stream-water concentrations of atrazine are depicted in figure 15. Stream-water concentrations of atrazine tend to be higher than pore-water concentrations at the same site (fig. 16) However, the concentrations that were below detection were not included in figure 16. When these concentrations are taken into account the mean stream water atrazine concentration was 0.18 ± 0.18 ppb, while the mean pore water atrazine concentration is 0.17 ± 0.15 ppb, indicating that there is no actual difference between atrazine concentrations in pore water and surface water.

Atrazine Detection Method Comparison

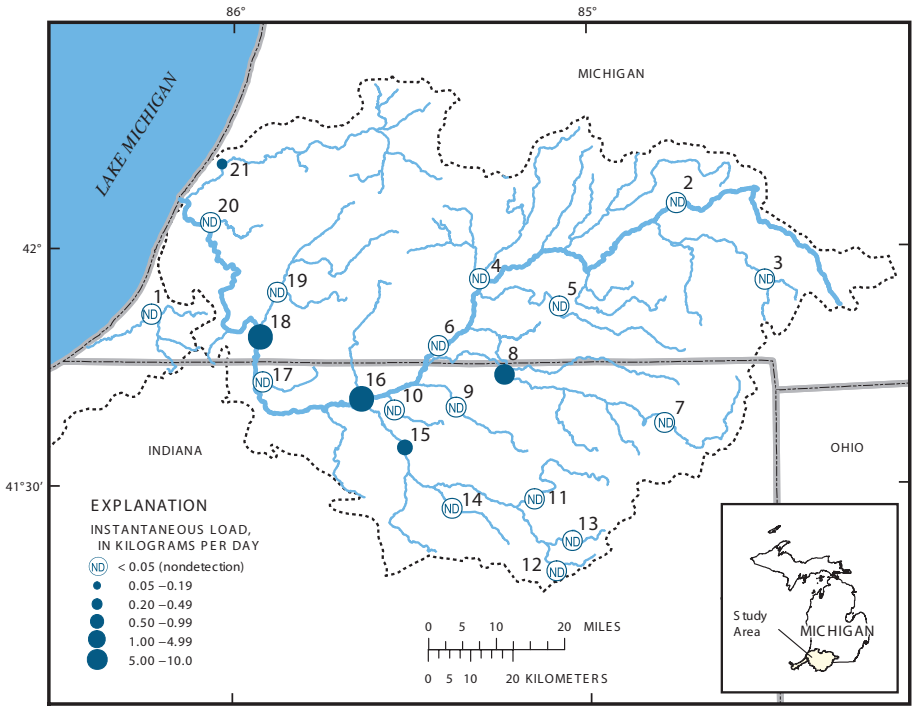
The concentrations of atrazine and related triazine compounds are summarized in table 2. The field result (ELISA) for the Pigeon River near Scott, Ind., (site 8) in July 2001 was 2 ppb, and the laboratory result was 0.654 ppb. The field result for the sample collected at Solomon Creek near Syracuse, Ind., (site 14) was 0.05 ppb, and the corresponding laboratory result was 0.122 ppb. The 2-ppb concentration for the sample from the Pigeon River was quite high compared to the other samples collected in July, and there may have been an analytical error. The Solomon Creek sample results are more consistent. For the East Branch Galien River at Gardener Road near Glendora, Mich., (site 46) the field value was 0.12 ppb, whereas the lab result was 0.085 ppb; and for the Galien River near Sawyer, Mich., (site 1) the field value was 0.08 ppb and the lab value was 0.043 ppb.

The average field concentration of atrazine at the four sites tested with both methods was 0.56 ppb, whereas the average laboratory concentration for all of the field-screen detected derivatives and other triazine pesticides for the same four sites was 0.23 ppb. The fact that the field concentration is higher is expected because the field method detects many atrazine derivatives and breakdown products, whereas the laboratory analysis is specific for atrazine and three related triazines. However, the presence of atrazine in field tests was verified by laboratory analysis in every comparison. Additional water quality data and laboratory results of pesticide screen are presented in tables 3 and 4 respectively.



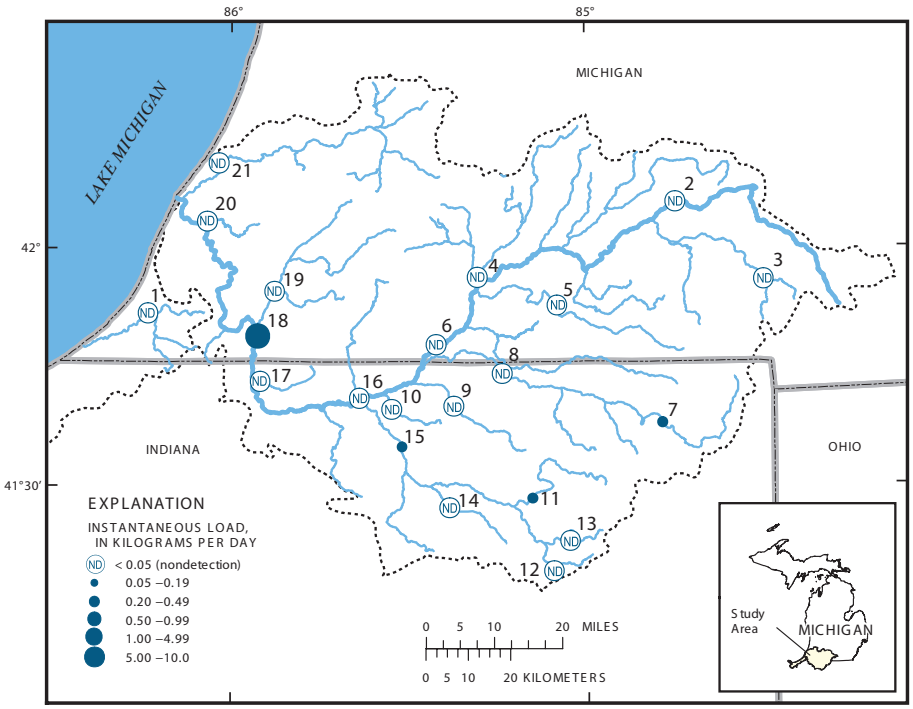
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 7. Instantaneous loads of atrazine in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, May 2001.



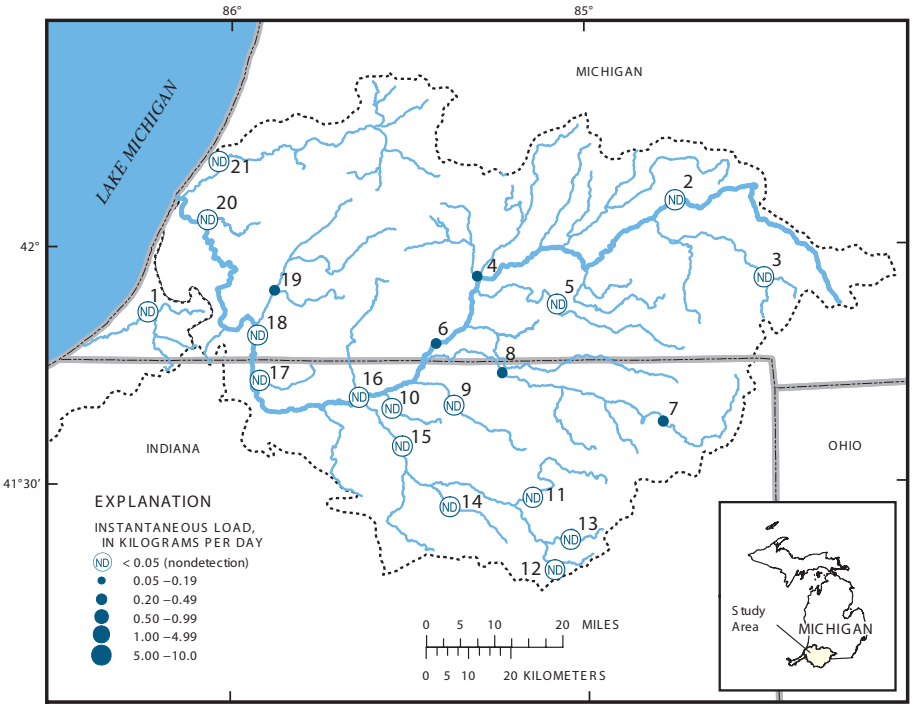
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 8. Instantaneous loads of atrazine in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, July 2001.



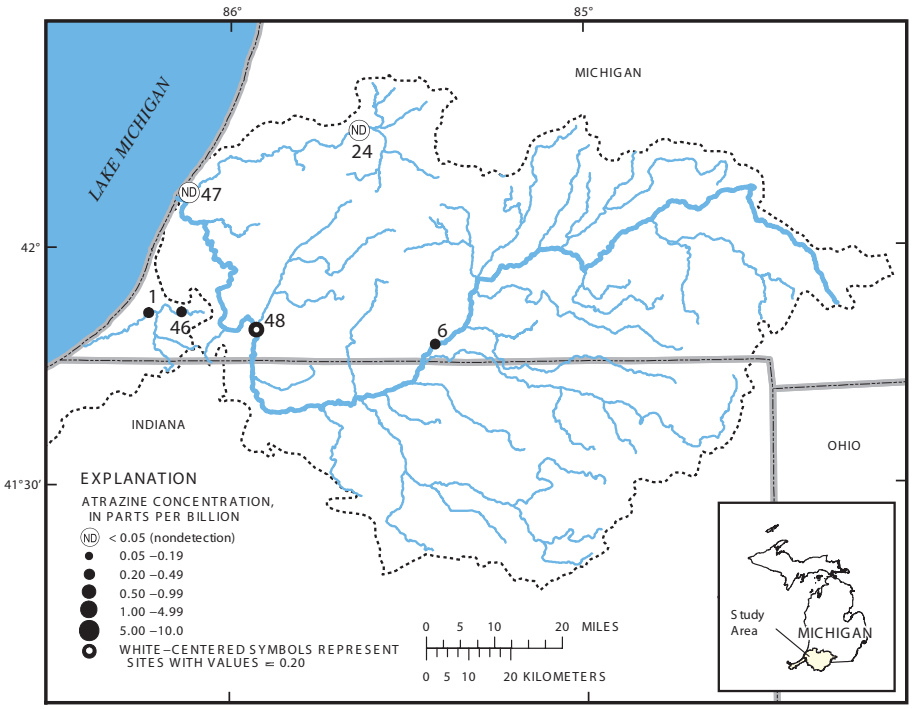
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 9. Instantaneous loads of atrazine in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, April 2002.



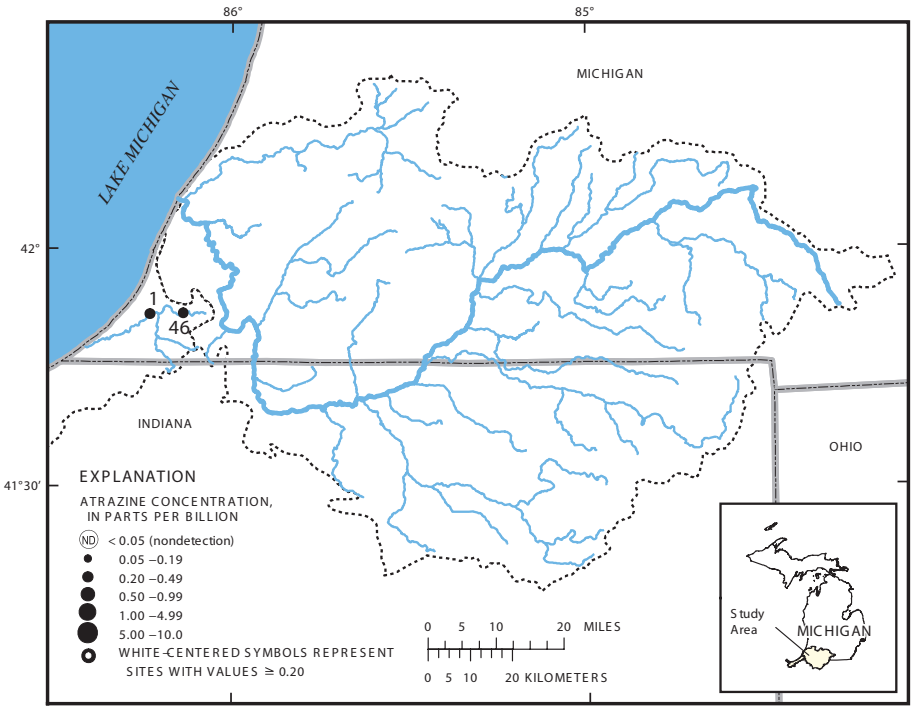
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 10. Instantaneous loads of atrazine in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, August 2002.



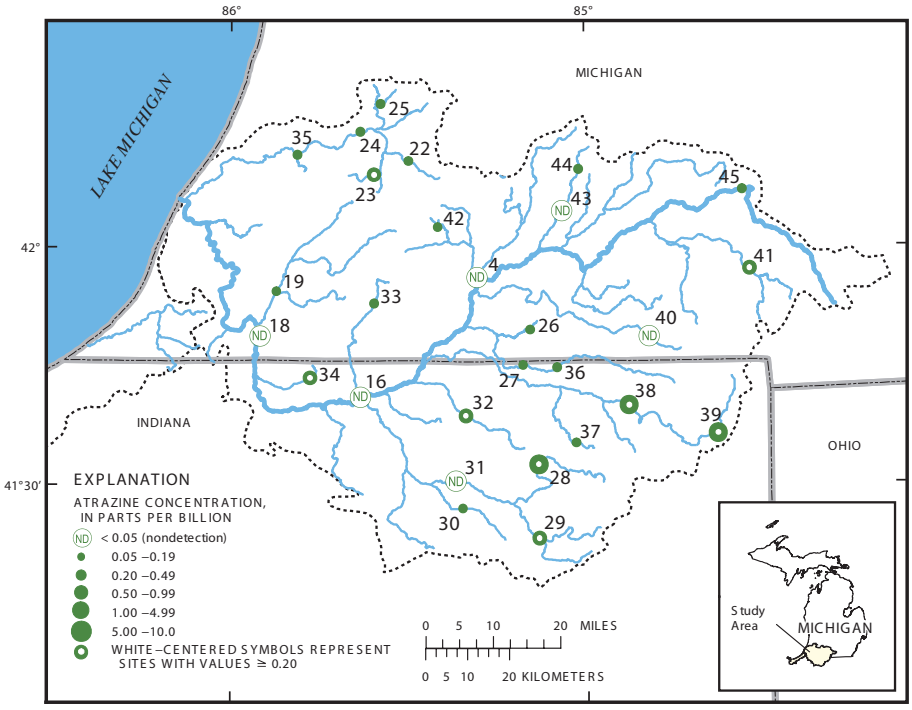
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 11. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, August 2003. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.



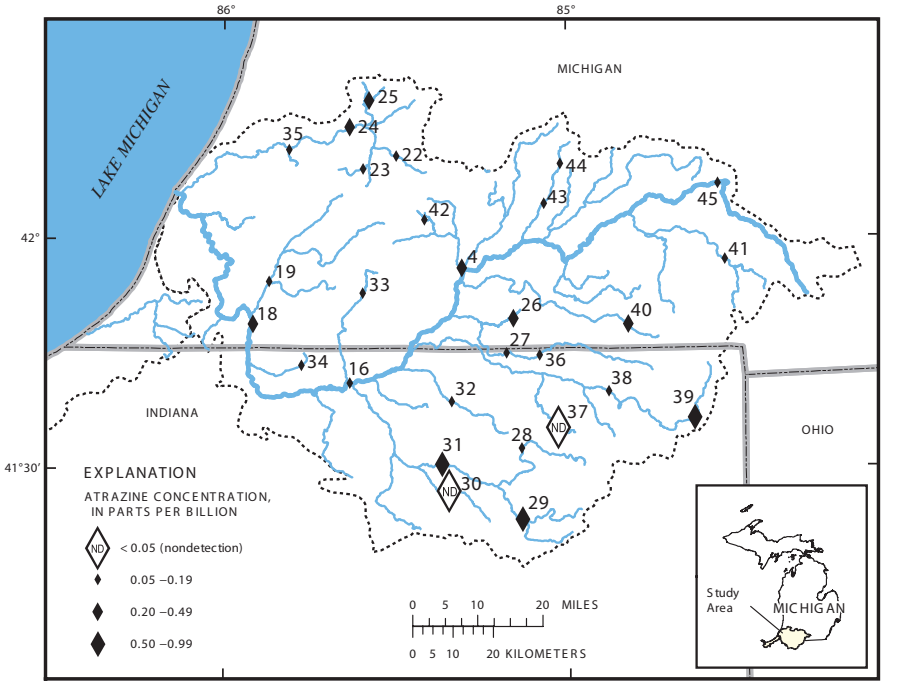
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 12. Atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, September 2003. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.



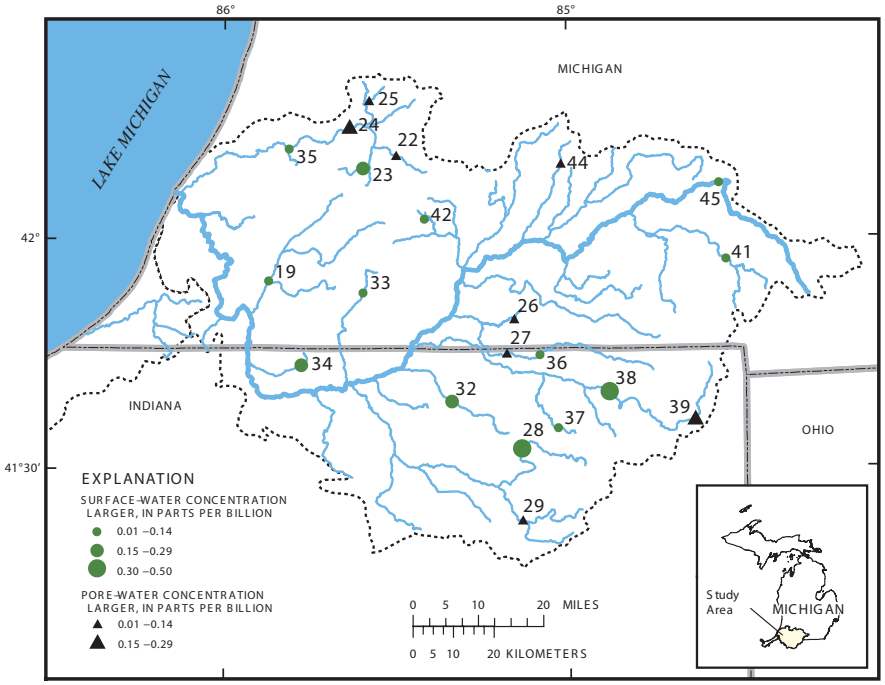
Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 13. Mean atrazine concentrations in stream water in the St. Joseph and Galien River Basins, Michigan and Indiana, September 2002. White centered symbols represent atrazine concentrations that exceed the amount determined to feminize frog populations.



Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 14. Mean atrazine concentrations in streambed sediment pore water in the St. Joseph and Galien River Basins, Michigan and Indiana, September 2002.



Base from U.S. Environmental Protection Agency, Office of Science and Technology, Reach File 1 for Conterminous United States in BASINS, 1:250,000, 1994
U.S. Environmental Protection Agency, Office of Water/OST, Hydrologic Unit Boundaries of the Conterminous United States in BASINS, 1:250,000, 1998
Michigan GeoRef Projection

Figure 15. Difference between atrazine concentrations in stream water and streambed sediment pore water in the St. Joseph and Galien River Basins, Michigan and Indiana, September 2002.

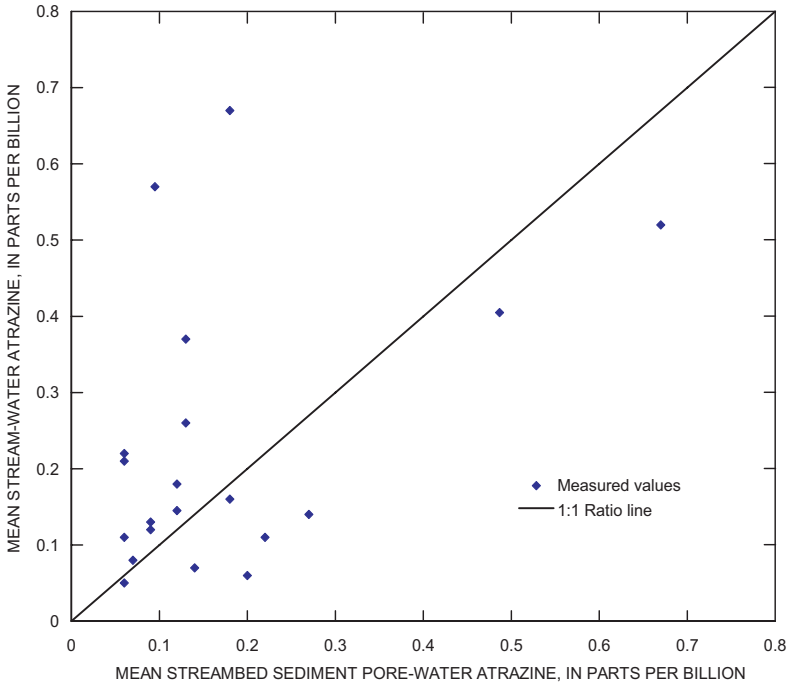


Figure 16. Relation of pore-water to stream-water atrazine concentrations in the St. Joseph and Galien River Basins, Michigan and Indiana, September 2002.

Table 2. Comparison of field ELISA triazine screen and laboratory C-18 chromatography atrazine results.
[abbreviations; USGS, U.S. Geological Survey]

USGS station name	USGS station number	Map number	Date sampled	Triazine screen (Field)	Triazine screen (Lab)*
Pigeon River near Scott, Ind.	04099750	8	7/10/2001	2.00	0.655
Solomon Creek near Syracuse, Ind.	04100377	14	7/11/2001	.05	0.126
East Branch Galien River at Gardener Road near Glendora, Mich.	04095995	46	9/2/2003	.12	0.087
Galien River near Sawyer, Mich.	04096015	1	9/2/2003	.08	0.051

*This accounts for all compounds in schedule 2001 that fall into the triazine screen. These include:
For the Triazine Field Screen: Atrazine, propazine, ametryn, prometryn, prometon, desethyl atrazine, terbutryn, terbutylazine, simazine, desisopropyl atrazine, cyanazine and 2-hydroxy atrazine.
Schedule 2001 includes: atrazine, cyanazine, prometon, simazine.

Table 3. Additional water-quality data in the St. Joseph and Galien River Basins, Michigan and Indiana
[abbreviations; USGS, U.S. Geological Survey; ND, nondetection; 1, not measured]

USGS Station Number	USGS Station Name	Date	Discharge	Dissolved Oxygen	pH	Specific Conductance	Temperature	Triazine Screen	
								Stream water	Pore water
			(ft^3/s)	(mg/L)	pH units	(µS/cm)	(Deg. C)	(µg/L)	(µg/L)
04102240	Brandywine Creek at 37th Street near Gobles, MI	8/26/2002	-	-	-	-	-	0.14	0.27
04099962	Christiana Creek at Brownsville Street near Vandalia, MI	8/28/2002	-	-	-	-	-	.12	.09
04101800	Dowagiac River at Sumnerville, MI	8/28/2002	-	-	-	-	-	.11	.06
04101800	Dowagiac River at Sumnerville, Mich.	5/21/2001	207.00	8.43	7.84	520.0	16.94	.09	-
04101800	Dowagiac River at Sumnerville, Mich.	7/11/2001	150.00	6.35	8.49	-	22.86	.08	-
04101800	Dowagiac River at Sumnerville, Mich.	4/15/2002	343.00	10.65	7.81	191.0	16.55	ND	-
04101800	Dowagiac River at Sumnerville, Mich.	8/6/2002	209.00	7.55	7.67	518.0	20.81	.13	-
04102139	Eagle Lake Drain at 39th Street near Lawton, MI	8/26/2002	-	-	-	-	-	.22	.06
04095995	East Branch Galien River at Gardener Road near Glendora, Mich.	8/19/2003	-	6.77	8.38	602.8	18.29	.10	-
04095995	East Branch Galien River at Gardener Road near Glendora, Mich.	9/2/2003	-	7.49	8.27	565.8	17.34	.12	-
04102172	East Branch Paw Paw River at 28th Street near Mattawan, MI	8/26/2002	-	-	-	-	-	.16	.18
04100500	Elkhart River at Goshen, Ind.	5/25/2001	414.00	10.12	7.91	616.0	15.34	.52	-
04100500	Elkhart River at Goshen, Ind.	7/9/2001	333.00	6.08	6.71	13.0	27.40	.38	-
04100500	Elkhart River at Goshen, Ind.	4/17/2002	1420.00	9.73	7.90	572.0	20.00	.05	-
04100500	Elkhart River at Goshen, Ind.	8/7/2002	177.00	7.92	7.20	652.0	23.20	.10	-
04100372	Elkhart River at Highway 13 near Millersburg, IN	8/27/2002	-	-	-	-	-	.03	.51
04098325	Fawn River at 125 East Road near Howe, IN	8/29/2002	-	-	-	-	-	.08	.07
04098465	Fawn River at 400 West Road near Scott, IN	8/29/2002	-	-	-	-	-	.07	.14
04099662	Fly Creek at County Road 400 East near LaGrange, IN	8/29/2002	-	-	-	-	-	.05	ND
04100252	Forker Creek near Burr Oak, Ind.	5/25/2001	10.00	8.35	7.66	428.0	18.33	.20	-
04100252	Forker Creek near Burr Oak, Ind.	7/10/2001	2.60	6.11	5.29	456.0	25.37	.76	-
04100252	Forker Creek near Burr Oak, Ind.	4/17/2002	28.00	10.38	8.07	440.0	19.57	ND	-
040973493	Four County Drain at Bowers Road near Flowerfield, MI	8/30/2002	-	-	-	-	-	.15	.12
04096015	Galien River near Sawyer, Mich.	5/22/2001	83.40	8.68	7.68	537.0	14.71	5.95	-
04096015	Galien River near Sawyer, Mich.	7/11/2001	29.10	6.48	8.12	-	23.68	.19	-
04096015	Galien River near Sawyer, Mich.	4/16/2002	80.30	7.86	7.41	577.0	16.19	ND	-
04096015	Galien River near Sawyer, Mich.	8/6/2002	19.60	8.82	7.54	620.0	19.69	ND	-
04096015	Galien River near Sawyer, Mich.	8/19/2003	-	7.69	8.32	623.1	18.21	.06	-
04096015	Galien River near Sawyer, Mich.	9/2/2003	-	8.28	7.50	560.4	16.26	.08	-
04102405	Hog Creek at 62nd Street near Hartford, MI	8/28/2002	-	-	-	-	-	.13	.09
414331086063801	Juday Creek at Bittersweet Road near Granger, IN	8/28/2002	-	-	-	-	-	.21	.06
04101370	Juday Creek near South Bend, Ind.	5/21/2001	10.00	8.99	8.02	712.0	17.92	.07	-
04101370	Juday Creek near South Bend, Ind.	7/11/2001	7.10	-	-	0.0	24.33	ND	-
04101370	Juday Creek near South Bend, Ind.	4/15/2002	25.00	11.84	8.08	726.0	18.55	ND	-
04101370	Juday Creek near South Bend, Ind.	8/6/2002	7.70	8.25	8.01	708.0	22.35	ND	-
04099804	Little Elkhart River at 50 North Road near Middlebury, IN	8/27/2002	-	-	-	-	-	.37	.13
04099808	Little Elkhart River at Middlebury, Ind.	5/24/2001	70.00	8.54	7.82	662.0	11.95	.09	-
04099808	Little Elkhart River at Middlebury, Ind.	7/9/2001	37.00	6.92	8.59	14.0	26.83	ND	-
04099808	Little Elkhart River at Middlebury, Ind.	4/17/2002	116.00	8.41	7.74	723.0	15.23	ND	-
04099808	Little Elkhart River at Middlebury, Ind.	8/7/2002	43.00	8.20	7.80	696.0	19.07	ND	-
04097060	Little Portage Creek at 38th Street near Fulton, MI	8/30/2002	-	-	-	-	-	ND	.10

Table 3. Additional water-quality data in the St. Joseph and Galien River Basins, Michigan and Indiana--Continued

Station ID	Station Name	Date	Discharge (ft^3/s)	Dissolved Oxygen (mg/L)	pH pH units	Specific Conductance (µS/cm)	Temperature (Deg. C)	Triazine Screen: Stream water (µg/L)	Triazine Screen: Pore water (µg/L)
04097038	Little Portage Creek at S Avenue near Climax, MI	8/30/2002	-	-	-	-	-	.05	.06
04100122	North Branch Elkhart River at 700 South Road near Eddy, IN	8/27/2002	-	-	-	-	-	.67	.18
04100222	North Branch Elkhart River at Cosperville, Ind.	5/25/2001	72.00	7.59	7.86	541.0	16.40	.18	-
04100222	North Branch Elkhart River at Cosperville, Ind.	7/10/2001	34.00	5.60	11.53	12.0	31.96	.36	-
04100222	North Branch Elkhart River at Cosperville, Ind.	4/17/2002	407.00	9.54	8.03	538.0	18.56	.06	-
04100222	North Branch Elkhart River at Cosperville, Ind.	8/14/2002	30.00	3.92	6.34	493.0	22.29	.39	-
04102324	Paw Paw River at 44th Avenue near Paw Paw, MI	8/26/2002	-	-	-	-	-	.06	.20
04102324	Paw Paw River at 44th Avenue near Paw Paw, Mich.	8/18/2003	-	7.84	7.80	485.4	21.84	ND	-
04102521	Paw Paw River at North Shore Drive, near Benton Harbor, Mich.	8/19/2003	-	7.10	7.84	517.3	20.15	ND	-
04102500	Paw Paw River at Riverside, Mich.	5/22/2001	337.00	7.94	7.80	500.0	16.70	ND	-
04102500	Paw Paw River at Riverside, Mich.	7/12/2001	231.00	7.25	6.74	519.0	20.32	.19	-
04102500	Paw Paw River at Riverside, Mich.	4/15/2002	650.00	12.13	8.13	469.0	16.65	ND	-
04102500	Paw Paw River at Riverside, Mich.	8/6/2002	291.00	6.84	7.49	476.0	21.60	ND	-
04099522	Pigeon Creek at County Road 1175E near Orland, IN	8/29/2002	-	-	-	-	-	.57	.01
04099510	Pigeon Creek near Angola, Ind.	5/23/2001	95.00	9.64	8.09	726.0	19.83	.78	-
04099510	Pigeon Creek near Angola, Ind.	7/9/2001	37.00	9.81	5.98	13.0	30.81	.55	-
04099510	Pigeon Creek near Angola, Ind.	4/17/2002	312.00	11.82	7.99	541.0	17.33	.10	-
04099510	Pigeon Creek near Angola, Ind.	8/14/2002	27.00	8.41	6.02	577.0	24.31	1.14	-
04099070	Pigeon Creek near Hamilton, IN	8/29/2002	-	-	-	-	-	0.52	0.67
04099750	Pigeon River near Scott, Ind.	5/23/2001	309.00	9.32	8.03	630.0	17.92	.33	-
04099750	Pigeon River near Scott, Ind.	7/9/2001	179.00	7.18	6.18	13.0	29.93	2.09	-
04099750	Pigeon River near Scott, Ind.	4/17/2002	840.00	7.64	7.82	574.0	18.67	ND	-
04099750	Pigeon River near Scott, Ind.	8/7/2002	140.00	8.67	7.92	588.0	22.13	.21	-
04099850	Pine Creek near Elkhart, Ind.	5/24/2001	11.00	9.27	7.91	675.0	12.71	.19	-
04099850	Pine Creek near Elkhart, Ind.	7/10/2001	5.90	8.02	12.80	14.0	-	.10	-
04099850	Pine Creek near Elkhart, Ind.	4/17/2002	21.00	9.42	7.42	688.0	14.94	ND	-
04099850	Pine Creek near Elkhart, Ind.	8/7/2002	16.00	10.20	7.40	685.0	19.89	ND	-
04100295	Rimmell Branch near Albion, Ind.	5/25/2001	8.80	9.99	7.55	724.0	12.79	2.80	-
04100295	Rimmell Branch near Albion, Ind.	7/11/2001	1.70	7.42	7.91	722.0	27.00	.27	-
04100295	Rimmell Branch near Albion, Ind.	4/17/2002	-	11.40	7.77	547.0	16.64	ND	-
04098610	Sherman Mill Creek at Sherman Mills Road near Sturgis, MI	8/27/2002	-	-	-	-	-	0.11	.22
041003747	Solomon Creek at County Road 43 near Ligonier, IN	8/27/2002	-	-	-	-	-	0.08	ND
04100377	Solomon Creek near Syracuse, Ind.	5/24/2001	31.00	7.76	7.58	748.0	12.06	.07	-
04100377	Solomon Creek near Syracuse, Ind.	7/10/2001	39.00	7.12	9.15	42.0	29.10	.05	-
04100377	Solomon Creek near Syracuse, Ind.	4/17/2002	81.00	10.38	7.43	738.0	15.67	ND	-
04100377	Solomon Creek near Syracuse, Ind.	8/14/2002	8.80	9.21	6.68	719.0	-	ND	-
04100303	South Branch Elkhart River at River Road near Albion, IN	8/27/2002	-	-	-	-	-	0.405	.49
04096520	South Branch Hog Creek at Boone Road near Quincy, MI	8/29/2002	-	-	-	-	-	0.26	.13
04096515	South Branch Hog Creek near Allen, Mich.	5/23/2001	72.60	7.32	7.58	497.0	14.53	1.34	-
04096515	South Branch Hog Creek near Allen, Mich.	7/13/2001	9.60	7.42	6.73	569.0	18.16	.50	-
04096515	South Branch Hog Creek near Allen, Mich.	4/16/2002	82.10	8.28	7.55	473.0	18.29	.20	-
04096515	South Branch Hog Creek near Allen, Mich.	8/14/2002	5.65	8.70	7.88	570.0	22.84	.08	-
04096405	St. Joseph River at Burlington, Mich.	5/23/2001	482.00	8.47	7.55	535.0	14.18	2.11	-
04096405	St. Joseph River at Burlington, Mich.	7/13/2001	93.40	8.67	7.61	268.0	19.60	.19	-
04096405	St. Joseph River at Burlington, Mich.	4/16/2002	333.00	8.85	7.93	538.0	19.77	ND	-
04096405	St. Joseph River at Burlington, Mich.	8/7/2002	73.80	7.84	7.55	629.0	19.15	.09	-
04096405	St. Joseph River at Burlington, Mich.	8/14/2002	60.40	7.76	7.40	9.0	21.79	.06	-
04101000	St. Joseph River at Elkhart, IN	8/28/2002	-	-	-	-	-	ND	.19
04101000	St. Joseph River at Elkhart, Ind.	5/24/2001	3880.00	8.00	7.90	527.0	17.53	.78	-
04101000	St. Joseph River at Elkhart, Ind.	7/10/2001	1670.00	6.76	12.97	33.0	30.16	.49	-
04101000	St. Joseph River at Elkhart, Ind.	4/17/2002	5800.00	9.81	8.03	536.0	19.19	ND	-
04101000	St. Joseph River at Elkhart, Ind.	8/6/2002	1430.00	7.54	7.89	604.0	25.75	ND	-
04099000	St. Joseph River at Mottville, Mich.	5/22/2001	2550.00	7.85	7.75	515.0	19.46	1.23	-
04099000	St. Joseph River at Mottville, Mich.	7/12/2001	793.00	6.64	7.01	481.0	25.46	ND	-
04099000	St. Joseph River at Mottville, Mich.	4/16/2002	3280.00	8.35	7.78	496.0	17.67	ND	-
04099000	St. Joseph River at Mottville, Mich.	8/7/2002	666.00	6.47	7.67	500.0	26.14	.05	-
04099000	St. Joseph River at Mottville, Mich.	8/18/2003	-	8.21	7.83	499.7	26.48	.09	-
04101500	St. Joseph River at Niles, MI	8/28/2002	-	-	-	-	-	ND	.22
04101500	St. Joseph River at Niles, Mich.	7/11/2001	1910.00	7.58	6.84	214.0	24.26	.28	-
04101500	St. Joseph River at Niles, Mich.	4/15/2002	6840.00	11.46	7.32	25.0	16.02	.08	-
04101500	St. Joseph River at Niles, Mich.	5/21/2002	6840.00	9.12	7.92	585.0	20.49	.58	-
04101500	St. Joseph River at Niles, Mich.	8/6/2002	1850.00	7.89	7.74	592.0	26.16	ND	-
04101501	St. Joseph River at Niles, Mich. (Auxiliary)	8/18/2003	-	7.61	8.02	596.0	25.82	.35	-
04097500	St. Joseph River at Three Rivers, Mich.	5/22/2001	1960.00	8.19	7.82	509.0	19.02	1.60	-
04097500	St. Joseph River at Three Rivers, Mich.	7/12/2001	576.00	7.40	7.47	140.0	26.01	ND	-
04097500	St. Joseph River at Three Rivers, Mich.	4/16/2002	2560.00	9.62	8.04	470.0	19.13	ND	-
04097500	St. Joseph River at Three Rivers, Mich.	8/7/2002	491.00	6.71	7.17	460.0	24.16	.08	-
04096340	St. Joseph River at Twenty-two Mile Road near Clarendon, MI	8/30/2002	-	-	-	-	-	0.18	.12

Table 4. Laboratory pesticide screen results in the St. Joseph and Galien River Basins, Michigan and Indiana

[µg/L, micrograms per Liter; mL, milliliters; micrometer, µm; --, not detected; E, estimated; fltrd, filtered; GF, glass filter]

Station number	Station name	Date	2,6-Diethylaniline water fltrd 0.7µm GF µg/L (82660)	CIAT, water, fltrd, µg/L (04040)	Acetochlor, water, fltrd, µg/L (49260)	Alachlor, water, fltrd, µg/L (46342)	alpha-HCH, water, fltrd, µg/L (34253)
04095995	E BRANCH GALIEN RIVER AT GARDNER RD NR GLENDORA,MI	09-02-03	<.006	E.0135	<.006	<.0045	<.0046
04096015	GALIEN RIVER NEAR SAWYER, MI	09-02-03	<.006	E.0081	<.006	<.0045	<.0046
04099750	PIGEON RIVER NEAR SCOTT, IN	07-10-01	<.0017	E.0473	.0123	<.0024	<.0046
04100377	SOLOMON CREEK NEAR SYRACUSE, IN	07-11-01	<.0017	E.0128	.0069	<.0024	<.0046

Station number	Date	alpha HCH-d6, surrog, water, fltrd, 0.7µm GF percent recovery (91065)	Atrazine, water, fltrd, µg/L (39632)	Azinphos-methyl, water, fltrd, 0.7µm GF µg/L (82686)	Benfluralin, water, fltrd 0.7µm GF µg/L (82673)	Butylate, water, fltrd, µg/L (04028)	Carbaryl, water, fltrd, 0.7µm GF µg/L (82680)	Carbofuran, water, fltrd, 0.7µm GF µg/L (82674)	Chlorpyrifos water, fltrd, µg/L (38933)	cis-Permethrin water, fltrd, 0.7µm GF µg/L (82687)	Cyanazine, water, fltrd, µg/L (04041)	DCPA, water, fltrd, 0.7µm GF µg/L (82682)
04095995	09-02-03	82.2807	.0706	<.05	<.010	<.002	<.041	<.020	<.005	<.006	<.018	<.0030
04096015	09-02-03	88.6957	.0270	<.05	<.010	<.002	E.0073	<.020	<.005	<.006	<.018	<.0030
04099750	07-10-01	104.673	.5040	<.0500	<.0100	<.0020	<.0410	<.0200	<.0050	<.0060	.0269	<.0030
04100377	07-11-01	100.000	.0802	<.0500	<.0100	<.0020	<.0410	<.0200	<.0050	<.0060	<.0180	<.0030

Station number	Date	Desulfinyl fipronil, water, fltrd, µg/L (62170)	Diazinon, water, fltrd, µg/L (39572)	Diazinon-d10 surrog. water, fltrd, 0.7µm GF percent recovry (91063)	Dieldrin, water, fltrd, µg/L (39381)	Disulfoton, water, fltrd, 0.7µm GF µg/L (82677)	EPTC, water, fltrd, 0.7µm GF µg/L (82668)	Ethalfluralin, water, fltrd, 0.7µm GF µg/L (82663)	Ethoprop, water, fltrd, 0.7µm GF µg/L (82672)	Desulfinyl-fipronil amide, water, fltrd, µg/L (62169)	Fipronil sulfide, water, fltrd, µg/L (62167)	Fipronil sulfone, water, fltrd, µg/L (62168)
04095995	09-02-03	<.004	<.005	123.6842	<.0048	<.021	<.0020	<.009	<.005	<.009	<.005	<.005
04096015	09-02-03	<.004	<.005	126.9565	<.0048	<.021	<.0020	<.009	<.005	<.009	<.005	<.005
04099750	07-10-01	--	<.0050	134.579	<.0048	<.0210	<.0020	<.0090	<.0050	--	--	--
04100377	07-11-01	--	.0071	131.132	<.0048	<.0210	<.0020	<.0090	<.0050	--	--	--

Table 4. Laboratory Pesticide Screen Results in the St. Joseph and Galien River Basins--Continued.

Station number	Date	Fipronil, water, fltrd, µg/L (62166)	Fonofos water, fltrd, µg/L (04095)	Lindane water, fltrd, µg/L (39341)	Linuron water, fltrd, 0.7µm GF µg/L (82666)	Malathion, water, fltrd, µg/L (39532)	Methyl parathion, water, fltrd, 0.7µm GF µg/L (82667)	Metolachlor, water, fltrd, µg/L (39415)	Metribuzin, water, fltrd, µg/L (82630)	Molinate, water, fltrd, 0.7µm GF µg/L (82671)	Napropamide, water, fltrd, 0.7µm GF µg/L (82684)	p,p'-DDE, water, fltrd, µg/L (34653)
04095995	09-02-03	<.007	<.0027	<.0040	<.035	<.027	<.006	.0260	<.006	<.0016	<.007	<.0025
04096015	09-02-03	<.007	<.0027	<.0040	<.035	<.027	<.006	.0331	<.006	<.0016	<.007	<.0025
04099750	07-10-01	--	<.0027	<.0040	<.0350	<.0270	<.0060	.0571	<.0060	<.0016	<.0070	<.0025
04100377	07-11-01	--	<.0027	<.0040	<.0350	<.0270	<.13	.0215	<.0060	<.0016	<.0070	<.0025

Station number	Date	Parathion, water, fltrd, µg/L (39542)	Pebulate, water, fltrd, 0.7µm GF µg/L (82669)	Pendimethalin, water, fltrd, 0.7µm GF µg/L (82683)	Phorate water, fltrd, 0.7µm GF µg/L (82664)	Prometon, water, fltrd, µg/L (04037)	Pronamide, water, fltrd, 0.7µm GF µg/L (82676)	Propachlor, water, fltrd, µg/L (04024)	Propanil, water, fltrd, 0.7µm GF µg/L (82679)	Propargite, water, fltrd, 0.7µm GF µg/L (82685)	Simazine, water, fltrd, µg/L (04035)	Tebuthiuron water, fltrd, 0.7µm GF µg/L (82670)
04095995	09-02-03	<.010	<.0041	<.022	<.011	<.015	<.0041	<.010	<.011	<.023	<.005	<.016
04096015	09-02-03	<.010	<.0041	<.022	<.011	<.015	<.0041	<.010	<.011	<.023	.0075	E.0101
04099750	07-10-01	<.0070	<.0016	<.0100	<.0110	E.0105	<.0041	<.0100	<.0110	<.0230	.0661	<.0160
04100377	07-11-01	<.0070	<.0016	<.0100	<.0110	<.0150	<.0041	<.0100	<.0110	<.0230	.0293	<.0160

Station number	Date	Terbacil, water, fltrd, 0.7µm GF µg/L (82665)	Terbufos, water, fltrd, 0.7µm GF µg/L (82675)	Thiobencarb water fltrd, 0.7µm GF µg/L (82681)	Triallate, water, fltrd, 0.7µm GF µg/L (82678)	Trifluralin, water, fltrd, 0.7µm GF µg/L (82661)	Sample volume, Schedule 2001, mL (99856)	Data base number	Medium code
04095995	09-02-03	<.034	<.017	<.0048	<.0023	<.009	873	01	9
04096015	09-02-03	<.034	<.017	<.0048	<.0023	<.009	866	01	9
04099750	07-10-01	<.0340	<.0170	<.0048	<.0023	<.0090	933	01	9
04100377	07-11-01	<.0340	<.0170	<.0048	<.0023	<.0090	946	01	9

Conclusions

The purpose of this study was to determine whether atrazine was present in stream water within the two basins and whether local high atrazine concentrations could be identified as a first step in understanding the relation of ground water and surface water in atrazine transport. Spatial and temporal variations of atrazine concentrations were examined, as well as methodologies to investigate pore-water/stream-water interactions. This work was conducted in cooperation with the Michigan Department of Environmental Quality.

Atrazine was detected in stream-water and streambed pore-water samples from the St. Joseph and Galien River Basin from 2001-2003. Stream-water concentrations tended to peak in late spring when the herbicide was applied, and they decline to nondetection before the following spring planting. More work would be needed to relate agricultural management and herbicide application timetables, to observed atrazine concentrations in the St. Joseph and Galien River Basins.

No strong spatial relation between pore-water and stream-water atrazine concentrations was determined. Atrazine was detected in streambed sediment pore water at several sites across both basins, and the average of all pore-water atrazine concentrations was approximately equal to the average of all stream-water atrazine concentrations. However, the pattern of atrazine concentrations in the pore water and stream water suggested a potentially complex pore-water/stream-water relation that would require future studies to quantify.

To assess the precision of the field (ELISA) analyses, atrazine concentrations determined in 2001 and 2003 were verified by means of laboratory analysis. Some variation in these two analytical approaches is expected because the field atrazine screen also detects atrazine breakdown products; in most cases, the field-test concentrations were higher than the corresponding concentrations from the laboratory analysis. However, the presence of atrazine in field tests was verified by laboratory analysis in every comparison made.

The atrazine concentration at many sites (16 in May 2001; 9 in July 2001; 1 in April 2002; 3 in August 2002; 8 in September 2002 and 1 in August 2003) exceeded the concentration of atrazine that has been shown to feminize frog populations (0.2 ppb).

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